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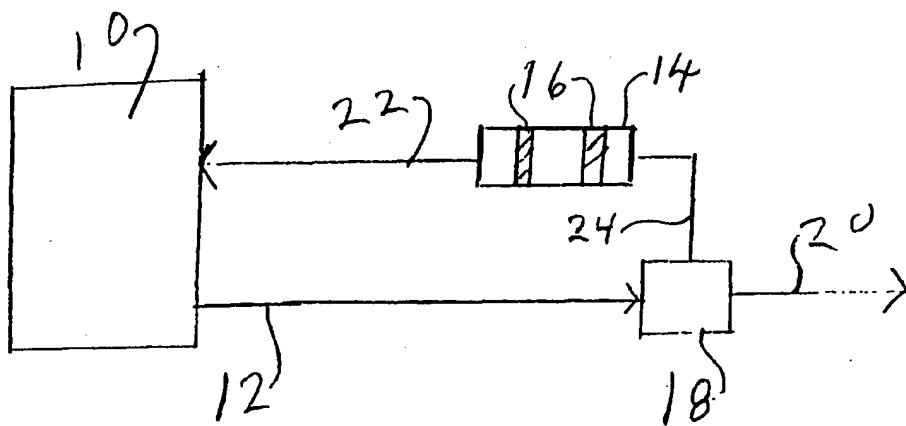
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(54) Title: REMOVAL OF SULFUR OXIDES FROM EXHAUST GASES OF COMBUSTION PROCESSES



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(57) Abstract: An oxidation catalyst/sorber (16) in a gas exhaust recirculation (EGR) system of an internal combustion engine (10) is provided to remove sulfur oxides out of the exhaust gas and is positioned within the EGR loop (22) in a form of allow rapid circulation. The oxidation catalyst comprises at least one component containing either Pt, Pd, Rh, Ru, Ni, Fe, Cu, Mo, Co or Mn and mixtures and combinations thereof, and the oxidation catalyst is supported on a support, such as alumina, silica, silica-alumina, titania and zirconia. The oxidation catalyst is in close proximity to a sorber, such as metal carbonate, which reacts with the SO₂ and/or SO₃ to form sulfites or sulfates.

REMOVAL OF SULFUR OXIDES FROM EXHAUST GASES OF COMBUSTION PROCESSES

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to the removal of gaseous sulfur compounds from gaseous streams, particularly the removal of SO_2 from combustion and industrial process effluents wherein an exhaust gas recirculation (EGR) system is used.

Related Art

As one result of concern with air pollution, environmental regulators have severely reduced and are continuing to reduce allowable emissions of sulfur oxides and hydrogen sulfide. As a result, a variety of technologies have been developed and are continuing to be developed for use in flue gas desulfurization (FGD). Internal combustion engines are one source of the emission of such sulfur compounds because of sulfur-containing compounds in fuel.

It is highly desirable to effectively remove sulfur compounds at process conditions in a selective manner, i.e., remove sulfur species without interference from organic or other combustion species, and with a physically durable system with low resistance to flow. Such technology would be useful for removing sulfur compounds from the exhaust gas recirculation loop of mobile combustion engines and the exhaust of mobile and stationary combustion engines.

Requirements for NO_x reduction from diesel engine exhaust can be met by using exhaust gas recirculation (EGR). Unfortunately, the high levels of sulfur to be recycled can increase the rate of corrosion of engine components. It would therefore be desirable to remove the sulfur containing compounds.

Current technologies capable of removing sulfur compounds from combustion exhaust include the use beds of activated carbon, potassium permanganate, wet scrubbers or dry scrubbers. Each of these technologies has limitations, not the least of which are enumerated below:

1. Activated or impregnated carbon cannot be used at high temperatures (>300°F) in an oxidizing environment due to carbon combustibility. Carbon is a soft, weak material with poor durability.

5 targets of such a system are different from the prior art. First, there is no need for in situ regeneration. Second, reusability of the system is desirable but not required.

10 These considerations open opportunities in system design. For example, oxidation catalysts and sorbents need not withstand the rigors of oxidation and reduction. Solid state reactions between sorbent and catalyst supports which would have damaged performance caused by cyclic oxidation-reduction and temperature are no longer damaging but can be beneficial for increased capacity. The use of an oxidation catalyst/sorber catalyst in an EGR system is not disclosed in the prior art.

15 **SUMMARY OF THE INVENTION**

Briefly, the present invention is the use of an oxidation catalyst/sorber in a gas exhaust recirculation (EGR) system or loop of an internal combustion engine. The oxidation catalyst/sorber is positioned within the EGR loop in a form to allow rapid circulation through and in contact with the oxidation catalyst/sorber. The 20 oxidation catalyst is preferably deposited on a high support area which is preferably intimately associated with the sorber. The oxidation catalyst/sorber is preferably deposited on a carrier.

BRIEF DESCRIPTION OF THE DRAWING

25 The figure is a schematic diagram of an EGR loop using an oxidation catalyst/sorber to remove SO_x from exhaust gas.

DETAILED DESCRIPTION

In a preferred embodiment of the present invention, the oxidation catalyst component is dispersed on a high surface area support. An inorganic compound which will react with SO_x compound, preferably inorganic compounds which will react or combine completely with SO_2 and/or SO_3 to form sulfites or sulfates, is 30 added to the catalyst component. In a more preferred embodiment, the inorganic compounds are dispersed uniformly and in close proximity to the catalyst component and more preferably the two are intimately associated, preferably by coating the sorber over the oxidation catalyst or supported oxidation catalyst. The 35 oxidation catalyst/sorber can be coated onto a ceramic or metal substrate or formed, for example, into a pellet, sphere or polylobe. The significance of the shape is to optimize gas contact.

5 The inorganic compounds may be deposited in micropores on the high
 surface area support. During reaction with sulfur oxides, it is highly desirable that
 relatively large volumes of sulfur oxides be reacted and also that the products of
 reaction not expand to constrict the porosity or cause stress and breakage of the
 high surface area support. Table 1 list several examples of inorganic compounds
 10 which are suitable for the present invention.

Table 1

Inorganic Compounds Useful for Reacting with Oxides of Sulfur

	SORBER	MW Sulfate	MW SO ₂	%SO ₂	Density Carbonate	Density Sulfate	Density Oxide	Density Hydroxide
15	Li ₂ CO ₄	109.95	64	58.2%	2.110	2.210	2.013	1.450
	Na ₂ CO ₄	142.04	64	45.1%	2.540	2.700	2.270	2.130
	K ₂ CO ₄	174.26	64	36.7%	2.290	2.660	2.350	2.044
	MgCO ₄	120.37	64	53.2%	3.050	2.660	3.600	2.370
	CaCO ₄	136.14	64	47.0%	2.830	2.960	3.340	2.200
20	SrCO ₄	183.68	64	34.8%	3.500	3.960	5.100	3.625
	BaCO ₄	233.39	64	27.4%	4.287	4.490	5.720	3.743
	Fe ₂ (CO ₄) ₃	399.88	192	48.0%	---	3.100	5.250	3.120
					Precursor Volume Carbonate	Precursor Volume Sulfate	Precursor Oxide	Precursor Hydroxide
25	SORBER	MW Sulfate	MW SO ₂	%SO ₂				
	Li ₂ CO ₄	109.95	64	58.2%	0.474	0.452	0.497	1.379
	Na ₂ CO ₄	142.04	64	45.1%	0.394	0.370	0.441	0.939
	K ₂ CO ₄	174.26	64	36.7%	0.437	0.376	0.426	0.978
	MgCO ₄	120.37	64	53.2%	0.328	0.376	0.278	0.422
30	CaCO ₄	136.14	64	47.0%	0.353	0.338	0.299	0.455
	SrCO ₄	183.68	64	34.8%	0.286	0.253	0.196	0.276
	BaCO ₄	233.39	64	27.4%	0.286	0.223	0.175	0.267
	Fe ₂ (CO ₄) ₃	399.88	192	48.0%	----	0.323	0.190	0.641

35 The oxidation catalysts may be any of those known in the art to oxidize
 organic sulfur compounds to the oxides, such as those disclosed in U.S. Pat. No.
 5,451,558, which is incorporated herein in its entirety and U.S. Pat. No. 6,037,307,
 which is incorporated herein in its entirety. Suitable oxidation catalysts include the
 noble metals, e.g., Pt, Pd, Rh, Ru, Ni, Fe, Cu, Mo, Co, Mn and mixtures and

5 combinations thereof. The oxidation catalysts may be prepared in any manner known in the prior art. The noble metals, particularly Pt are preferred.

The oxidation catalyst is preferably deposited on a high surface area support. The high surface area supports are typically alumina, silica, silica-alumina, titania or zirconia, and combinations thereof. Alumina is a preferred high surface area support. Generally, the surface area of high surface area supports is in the range of 40 to 350 m²/g, preferably 100 to 325 m²/g and more preferably 200 to 300 m²/g.

10 The sorber material may be any material which will react with or otherwise combine with SO_x (SO₂ and SO₃) to form stable compositions under the condition of the EGR loop. Included among these materials are the alkali metals, alkaline earth metals, Ti, Zr, Hf, Ce, Al, Si, Fe and mixtures and combinations thereof. Preferred sorbers include Li, Na, K, Mg, Ca, Sr, Ba, Fe and mixtures and combinations thereof. The sorber may be supplied to the oxidation catalyst as a variety of precursor, but is preferably converted to or deposited as the oxide, hydroxide or carbonate for use.

15 The supported oxidation catalyst/sorber may be extruded in a suitable form such as beads, spheres, loops, polylobes and the like or applied to a carrier. The carrier may be honeycombed ceramic, or expanded (foamed) metal generally known as monoliths. The carrier is preferably a macroporous material having from 20 64 to 600 cells (pores) per square such (CPS) which is about 25 to 80 pores per linear inch (ppi) although lower pore count materials are suitable.

20 The oxidation catalyst comprises from 0.25 to 50 wt%, preferably 0.5 to 20 wt% of the combination of oxidation catalyst and high surface area support. The sorbent comprises 1 to 50 wt%, preferably 10 to 30 wt% of the combination of catalyst, sorbent and high surface area support. When the oxidation catalyst/sorber is applied to a carrier, it comprises 1 to 50 wt %, preferably 10 to 30 wt% of the combination of oxidation catalyst/sorber and carrier.

25 The rate of flow of the gas in EGR loop will depend on many factors such as the sulfur compound content in the gas, the effectiveness of the oxidation catalyst/sorber, the temperature of the contacting, degree of contact between the gas and the oxidation catalyst/sorber to list a few. However, the preferred rate of contact is at a GHSV (gas hourly space velocity) in the range of 5,000 to 150,000

5 hr⁻¹, more preferably 20,000 to 60,000 hr⁻¹, at temperatures in the range of 300 to 1000°F, more preferably 750 to 900°F.

10 Referring now to the figure, the internal combustion engine 10 is shown attached via exhaust 12 to controller 18 of the type known in the art to selectively recycle a portion of the treated exhaust via line 24 to an exhaust treatment zone 14 in which two oxidation catalyst/sorber units are disposed and hence via line 22 to the engine for use in the combustion chamber as appropriate and to direct a portion into exit line 20. The arrows indicate the direction of gas flow. The units in this embodiment are ceramic monoliths coated with the oxidation catalyst/sorber. There may be only one such unit or two or more. The composition of the oxidation catalyst/sorber on each unit may be the same or different. Furthermore, the 15 composition of oxidation catalyst/sorber may vary within a single unit.

20 The treated exhaust gas in exit line 20 may be passed to the atmosphere or to other treatment zones, such as conventional catalytic converts and/or additional oxidation catalyst/sorber treatment zones (not shown). Moreover, two or more exhaust treatment zones may be arranged in parallel for alternate use when the oxidation catalyst/sorber is totally used up and SOx occurs.

25 In the preferred embodiment the high surface area material is sacrificed to sulfate formation after the inorganic precursor is consumed. The latent reactivity toward sulfur compounds is critical to achieving high sulfur oxide removal capacity.

Example 1

30 A washcoat solution of Al₂O₃/Pt is prepared. This is accomplished by the incipient method technique. This technique involves the addition of an aqueous platinum solution to the dry Al₂O₃ until reaching incipient wetness. The concentration of the aqueous platinum solution was adjusted to produce 1.6% platinum in the dried Al₂O₃/Pt. This solid is then calcined at 500°C for 1 hour. After cooling to room temperature, 7% acetic acid is added to the Al₂O₃/Pt. After ball mill overnight, the resulting washcoat solution contains 45% Al₂O₃/Pt with a particle size between 3 and 4 μm.

35 A 400 cpi honeycomb cordierite carrier is then dipped into the washcoat solution. After excess washcoat is blown off, the sample is dried at 150°C for 30 minutes and then calcined at 500°C for 1 hour. The washcoat loading is determined to be 2.5g/in³.

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5 A 45% lithium nitrate solution is prepared. The $\text{Al}_2\text{O}_3/\text{Pt}/\text{honeycomb}$ sample is then dipped into the 45% lithium nitrate. After excess solution is blown off, the sample is dried at 150°C for 30 minutes. The sample is then exposed to ammonia and carbon dioxide to convert the lithium nitrate to lithium carbonate, which has greater reactivity.

10 The oxidation catalyst/sorber is loaded into a laboratory reactor. The laboratory reactor simulates the exhaust gas of an internal combustion engine and consists of a sample tube furnace, compresses gas cylinders, steam tube furnace, flow controllers, flow traducers, chiller, stainless steel tubing, heating tape, and a Bovar sulfur dioxide analyzer interfaced to a PC for data acquisition.

15 The test conditions consist of a gas hourly space velocity of 10,000/hr, 550°F, 200 ppm SO_2 , 12% O_2 , 5% H_2O , and 8% CO_2 . The higher than typical sulfur dioxide concentration, 200 ppm, is utilized to accelerate the test. Previous work has demonstrated that this modification to simulated conditions has no effect on capacity or performance. The data is summarized in Table 2 and demonstrates that the process efficiently removes the sulfur dioxide for 260 minutes. In the 20 vicinity of 260 minutes, the sulfur dioxide begins to breakthrough.

Table 2.

	Time (Minutes)	SO_2 (ppm)
25	020	000
	044	000
	060	000
	080	000
	100	000
	120	000
30	140	000
	160	000
	180	000
	200	000
	220	000
	240	000
35	260	3.66
	280	8.54

5 Table 2 Continued

300	17.09
320	25.63

EXAMPLE 2

10 The carrier is 400 cpi honeycomb cordierite. A washcoat solution is prepared consisting primarily of high surface area alumina and deionized water. The alumina washcoat is wet milled overnight to obtain a particle size between 3 and 4 microns. The washcoat is then analyzed for solids content and diluted to about 45% solids content.

15 The 400 cpi honeycomb is dipped into the alumina washcoat. The excess washcoat is blown from the cells with compressed air. The 400 cpi piece is dried at 150°C for 30 minutes, then calcined at 500°C for 1 hour. After calcination the alumina washcoat loading is determined to be 2.3 grams/cubic inch.

20 A 26% $\text{Co}(\text{NO}_3)_2$ solution is prepared by dissolving 20.88 grams of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ into 29.12 grams of deionized water. The 400 cpi sample is then dipped into the 26% $\text{Co}(\text{NO}_3)_2$ solution. After the excess solution is blown from the cells, the sample is placed into a 150°C furnace for 20 minutes. Then the sample is calcined at 500°C for 1 hour. After calcination the elemental Co loading is determined to be 0.25 g/in.³ present as Co_2O_3 .

25 A 45% LiNO_3 solution is prepared. The $\text{Al}_2\text{O}_3/\text{Co}_2\text{O}_3/\text{honeycomb}$ sample is then dipped into the 45% LiNO_3 solution. After the solution is blown from the cells, the sample is dried at 150°C for 30 minutes. The sample is then exposed to a gas stream containing anhydrous ammonia and carbon dioxide.

30 The catalyst/sorber is loaded into a laboratory reactor. The reactor simulated the exhaust gas of an internal combustion engine and consists of a sample tube furnace, compressed gas cylinders, steam tube furnace, flow controllers, flow transducers, chiller, stainless steel tubing, heating tape, and a BOVAR sulfur dioxide analyzer which interfaces to a PC for data acquisition which is reported in Table 3.

35 The test conditions consist of a space velocity of 50,000/hr, 1000°F, 200 ppmv SO_2 , 12% O_2 , 8% CO_2 , and 5% H_2O . The SO_2 concentration of 200 ppmv is used to accelerate the test. Previous work has demonstrated that this modification to simulated conditions has no effect on capacity or performance. The data below

5 demonstrates that the base metal sulfur trap adsorbs 100% of the SO₂ initially, but the removal efficiency slowly decreases after about 4 minutes exposure to the 200 ppmv SO₂ at 50,000/hr space velocity. The base metal trap with Co₂O₃ converts only a minute amount of SO₂ to SO₃, which can and does erode stainless steel components from the reaction of SO₃ with H₂O to form sulfuric acid.

10

TABLE 3

	Time (minutes)	SO ₂ (ppmv)
	2	0
	5	7.32
	10	41.5
15	15	101.32
	20	119.63
	30	137.94
	40	144.04
	50	147.71
20	60	157.47
	80	164.80
	100	168.46
	120	173.34
	140	180.66
25	160	183.11
	180	189.21
	200	190.43
	220	194.09
	240	192.87
30	260	198.98

Example 3

A catalyst/sorber sulfur trap was prepared with the catalyst and sorber components on two separate carriers.

35 An alumina washcoat is prepared by adding enough alumina to an acidic solution to contain 45% solids. The washcoat is wet milled overnight until the particle size measured 3 to 4 microns in diameter. A 400 cpi ceramic honeycomb carrier is then dipped into the alumina washcoat. The excess washcoat is blown

5 from the cells with compressed air. Once the cells are clear, the sample is placed into a 150°C furnace for 30 minutes and calcined at 500°C for 1 hour. The alumina loading is determined to be 2.2 gr/in³.

10 After the sample has calcined, the sample is dipped into a platinum solution. The concentration of the solution is adjusted to give a platinum loading equivalent to 1.66% of the alumina weight. The excess solution is blown from the cells. The sample is then dried at 150°C for 30 minutes and calcined at 500°C for 1 hour.

15 The sorber is prepared on a second 400 cpi honeycomb carrier by dipping the carrier in the 45% alumina washcoat. The excess washcoat is blown from the cells. After the excess washcoat is removed, the sample is placed in the furnace to dry at 150°C for 30 minutes and calcined at 500°C for 1 hour. The washcoat loading is determined to be 2.46 g/in³. The lithium sorber coating is dispersed on top of the alumina. A 45 % lithium nitrate solution is prepared and the sample placed in the solution for 10 minutes. After 10 minutes, the sample is removed from the solution and the excess blown from the cells. The sample is heated at 20 150°C for 30 minutes. The carrier is wrapped with a high-temp aluminosilicate rope and placed into a stainless steel tube. A gas containing anhydrous ammonia and carbon dioxide is passed over the sample for about 10 minutes to precipitate the carbonate of lithium. The carrier is dried again at 150°C for 30 minutes and calcined at 500°C for 1 hour. The carrier contains a lithium loading of about 1.4% 25 of the total sorber/washcoat/carrier weight.

30 The dual catalyst/sorber samples are placed inside a stainless steel tube reactor with the oxidation catalyst placed in front, upstream of the sorber trap. The sample is subjected to a gas stream which closely simulates an exhaust gas stream of an internal combustion engine. The gas mixture contains 12% O₂, 8% C₀₂, and 5% H₂O. The level of S0₂ is 154 ppmv, which accelerates the point at which 100% breakthrough occurs. Previous data showed there is no decrease in capacity or adsorption efficiency by increasing S0₂ levels. The gas space velocity is 50,000/hr and the temperature is 1000°F. The S0₂ level is monitored using a BOVAR model 721-M Photometric S02 analyzer and the analyzer interfaced to a 35 PC for data acquisition.

The data in Table 4 demonstrates the S0₂ capacity achievable by the dual catalyst/sorber design.

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The data in Table 4 demonstrates the S0₂ capacity achievable by the dual catalyst/sorber design.

The invention claimed is:

1. An exhaust gas recirculation (EGR) system comprising:
an exhaust gas treatment zone having at least one oxidation catalyst/sorber unit disposed therein.
2. The EGR system according to claim 1 comprising:
an internal combustion engine, an exhaust connected to said exhaust gas treatment zone, and a controller for selectively recycling a portion of the exhaust gas from said exhaust gas treatment zone to said internal combustion engine to a combustion chamber thereof.
3. The EGR system according to claim 1 wherein said oxidation catalyst comprises Pt, Pd, Rh, Ru, Ni, Fe, Cu, Mo, Co, Mn and mixtures and combinations thereof deposited on a high surface area support and intimately associated with a sorber comprising an inorganic compound capable of combining with SO_x gases to form stable compositions.
4. The EGR system according to claim 3 wherein said high surface area support comprises alumina, silica, silica-alumina, titania, zirconia and mixtures and combinations thereof.
5. The EGR system according to claim 3 wherein said high surface area support comprises alumina.
6. The EGR system according to claim 3 wherein the inorganic compound comprises an alkali metal, an alkaline earth metal, Ti, Zr, Hf, Ce, Al, Si, Fe and mixtures and combinations thereof.
7. The EGR system according to claim 6 wherein the inorganic compound comprises Li, Na, K, Mg, Ca, Sr, Ba and Fe and mixtures and combinations thereof.
8. The EGR system according to claim 3 wherein said high surface area support comprises alumina, silica, silica-alumina, titania, zirconia and mixtures and combinations thereof and said inorganic compound comprises an alkali metal, an alkaline earth metal, Ti, Zr, Hf, Ce, Al, Si, Fe and mixtures and combinations thereof.
9. The EGR system according to claim 8 wherein said oxidation catalyst comprises from 0.25 to 50 wt% of combination of oxidation catalyst and high

surface area support and said sorbent comprises 1 to 50 wt% of the combination of oxidation catalyst, sorbent and high surface area support.

10. The EGR system according to claim 8 wherein said oxidation catalyst, high surface area support and sorbent are applied to ceramic or metal monolith having a honeycomb structure and comprised from 1 to 50 wt% of the total of the combination thereof with said carrier.

11. A process for treating exhaust gas to remove SO_x in an exhaust gas recirculation (EGR) system comprising:

passing exhaust gas into an exhaust gas treatment zone having at least one oxidation catalyst/sorber unit disposed therein.

12. The according to claim 11 wherein said oxidation catalyst comprises Pt, Pd, Rh, Ru, Ni, Fe, Cu, Mo, Co, Mn and mixtures and combinations thereof deposited on a high surface area support and intimately associated with a sorber comprising an inorganic compound capable of combining with SO_x gases to form stable compositions.

13. The process according to claim 12 wherein said high surface area support comprises alumina, silica, silica-alumina, titania, zirconia and mixtures and combinations thereof.

14. The process according to claim 12 wherein said high surface area support comprises alumina.

15. The process according to claim 12 wherein the inorganic compound comprises an alkali metal, an alkaline earth metal, Ti, Zr, Hf, Ce, Al, Si, Fe and mixtures and combinations thereof.

16. The process according to claim 15 wherein the inorganic compound comprises Li, Na, K, Mg, Ca, Sr, Ba and Fe and mixtures and combinations thereof.

17. The process according to claim 12 wherein said high surface area high surface area support comprises alumina, silica, silica-alumina, titania, zirconia and mixtures and combinations thereof and said inorganic compound comprises an alkali metal, an alkaline earth metal, Ti, Zr, Hf, Ce, Al, Si, Fe and mixtures and combinations thereof.

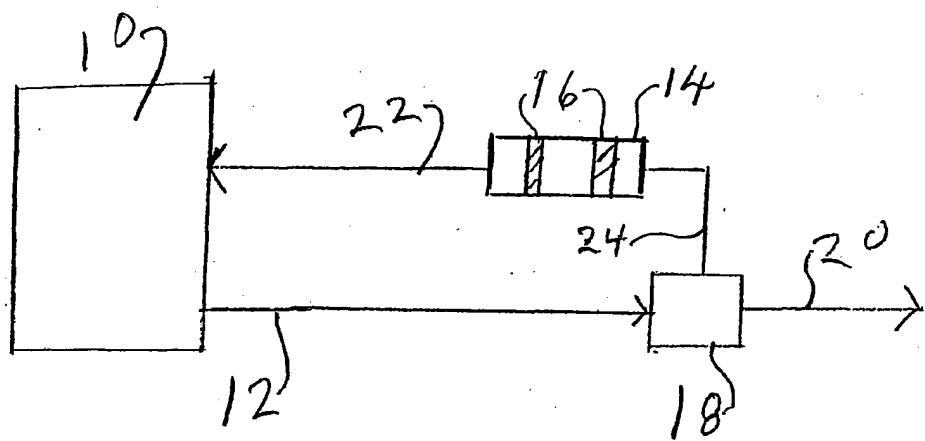
18. The process according to claim 13 wherein said oxidation catalyst comprises from 1 to 50 wt% of combination of oxidation catalyst and high surface

area support and said sorbent comprises 0.5 to 20 wt% of the combination of oxidation catalyst and sorbent.

19. The process according to claim 13 wherein said oxidation catalyst, high surface area support and sorbent are applied to ceramic or metal monolith having a honeycomb structure and comprised from 10 to 30 wt% of the total of the combination thereof with said carrier.

20. The process according to claim 11 wherein said exhaust gas is contacted with said oxidation catalyst/sorber unit at a GHSV in the range of 5,000 to 150,000 hr⁻¹.

21. The process according to claim 11 wherein said exhaust gas is contacted with said oxidation catalyst/sorber unit at a temperature in the range of 300 to 1,000°F.



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/42016

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :B01D 53/92, 53/94; F01N 8/10, 8/18, 8/20

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3,739,583 A (TOURTELLOTTE et al.) 19 June 1973, please see the figure and col. 2 ln. 50 to col. 7 ln. 17, especially col. 3 lns. 32-36, col. 3 lns. 55-58 and col. 4 ln. 17 to col. 5 ln. 17.	1-2
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Y	US 5,451,558 A (CAMPBELL et al.) 19 September 1995, please see col. 1 lns. 10-17, col. 2 lns. 38-45 and col. 3 lns. 17-22.	1-2
Y, P	US 6,272,848 B1 (OKUDE et al.) 14 August 2001, please see Fig. 4a and col. 22 ln. 53 to col. 28 ln. 22.	3-21
A, P	US 6,209,317 B1 (HIROTA) 03 April 2001, please see Fig. 1 and col. 8 ln. 64 to col. 10 ln. 9.	1-21

 Further documents are listed in the continuation of Box C. See patent family annex.

Special categories of cited documents:		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier document published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

05 OCTOBER 2001

Date of mailing of the international search report

16 NOV 2001

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/42015

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6,037,307 A (CAMPBELL et al.) 14 March 2000, please see col. 9 ln. 46 to col. 10 ln. 47.	1-21
A	US 5,650,127 A (CAMPBELL et al.) 22 July 1997, please see col. 8 ln. 38 to col. 10 ln. 16.	1-21
A	US 5,207,734 A (DAY et al.) 04 May 1993, please see Fig. 1 and col. 13 ln. 45 to col. 14 ln. 68.	1-21

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/42015

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

60/278, 297, 299, 302; 422/168, 171, 177, 180, 181, 234; 423/213.2, 213.5, 213.7, 244.01, 244.02, 244.04, 244.09, 244.10, 244.11, Dig. 5

B. FIELDS SEARCHED

Minimum documentation searched

Classification System: U.S.

60/278, 297, 299, 302; 422/168, 171, 177, 180, 181, 234; 423/213.2, 213.5, 213.7, 244.01, 244.02, 244.04, 244.09, 244.10, 244.11, Dig. 5